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<p>(54) Title: TEXTILE ARTICLES OR CLOTHING HAVING SUPER HYDROPHOBIC COATING (57) Abstract The present invention relates to textile articles and clothing such as outdoor garments, indoor garments exposed to aqueous liquid, swim wear, leather, hats, textile sun roofs for cars, sun blinds or awnings which have at least part of their surface provided with super hydrophobicity.</p>		

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**Textile articles or clothing**  
**having super hydrophobic coating**

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**Field of the invention**

The present invention relates to textile articles and clothing such as outdoor garments, indoor garments exposed to aqueous liquid, swim wear, shoes, leather, hats, textile sun roofs for cars, sun blinds or awnings which have at least part of their surface provided with super hydrophobicity.

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**Background of the invention**

For instance, U.S. Pat. No. 3,498,527 teaches that paper board containers for liquids can be waterproofed by application of a waterproofing coating such as wax or polyethylene, and a similar method is shown in U.S. Pat. No. 2,708,645 for waterproofing paper drinking cups and in U.S. Pat. No. 3,212,697 for paper grocery sacks. In U.S. Pat. No. 3,597,313, temporary wet strength is imparted to paper by coating it with a polymeric alcohol-polymeric aldehyde reaction product.

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Coating processes, by themselves, have been used to produce disposable articles of sanitary clothing. In U.S. Pat. No. 3,078,849, a disposable sanitary napkin is disclosed which consists of an adsorbent layer having a liquid-repellent backing of polyvinyl alcohol or similar material capable of initially repelling water but eventually solubilizing. The degree of water-repellency, therefore the lifetime of the napkin, is controlled by varying the thickness of the backing. Because the

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necessary life of the napkin cannot be predicted by manufacturer or user, the backing must be sufficiently thick to take account of all normal contingencies. U.S. Pat. No. 3,542,028 is directed to a flushable sanitary napkin consisting of a cellulosic sheet treated with a fluoropolymer coating. U.S. Pat. No. 3,559,650 teaches the preparation of a sanitary napkin having two flush-disposable sides separated by a waterproof film too thin to support itself once both faces of the napkin have disintegrated upon disposal.

Analogous to the process of coating a surface with a waterproofing substance is the concept of reacting a surface with another material so as to form a reaction product on the surface which has water-repellent properties. For example, U.S. Pat. Nos. 2,130,212 and 3,137,540 teach that materials such as polymeric alcohols may be reacted with other materials to increase their water-repellent properties. The latter patent teaches treating polyvinyl alcohol articles with an aqueous emulsion of an aldehyde to impart water-repellency thereto. U.S. Pat. No. 3,626,943 teaches that disposable diapers can be made from polyvinyl alcohol and waterproofed on one side by reaction with formaldehyde. These reaction-type coating processes suffer from drawbacks. They are carried out in the aqueous phase which is complicated and requires relatively large quantities of reagents. Most of the processes which employ some form of in situ chemical reaction to produce a water-repellent surface are carried out in the liquid phase, some vapor phase treatments are taught by U.S. Pat. Nos. 2,306,222; 2,961,388; and 3,017,290.

A known method of water and oil repellent finishing of textiles, described in USSR Patent 1,158,634, includes plasma treatment in a glow discharge in an atmosphere of inorganic gases, followed by treatment with a fluorine containing acrylic monomer in gas phase. Another prior method of achieving film plasma polymerization, described in U.S. Pat. No. 4,188,426, includes treatment in a glow discharge of per-fluoro-cyclo-butane or hexafluoroethane to reduce the friction coefficient and to improve the surface hydrophobia of organic and inorganic textile

substrates (e.g. polyethylene films, metals). However these disclosures do not achieve a level of water repellency as the present invention.

Plasma-deposited fluorocarbon coatings are often cited in the literature as "teflon-like coatings" because their  $CF_x$  ( $0 < x \leq 2$ ) composition and surface energy can be made very close to that of polytetrafluoroethylene (PTFE,  $-(CF_2-CF_2)_n$ ), known on the market as Teflon®.

Plasma coating processes of metals, polymers, and other textile substrates, with fluorocarbon films are known in the art. As an example, it is known from USP 4 869 922 and from other sources, that deposition from continuous (i.e. non modulated) radiofrequency (RF) glow discharges fed with fluorocarbons provides films, layers, tapes, plates, and differently shaped articles made of plastics, metals or other materials, with a thin fluorocarbon coating, with no other material interposed between the coating itself and the substrate. Such coatings are claimed to have very good adherence to the items processed, to be void-free, to be uniform or not porous, and to show controlled wettability characteristics, which depend on their surface chemical composition. The non modulated, continuous plasma process of the above mentioned patent leads to coatings characterized by static water contact angle (WCA) values lower than  $120^\circ$ .

Glow discharges treatments are also considered in US-A-5 462 781 for improving the bondability of an implantable polymer medical device or for changing the wettability of a polymer fabric. Several of the references discussed in this patent confirm non modulated, continuous plasma treatments as a means for varying the inherent WCA of a surface.

US-A-5 034 265 discloses a non modulated, continuous plasma treatment for improving the biocompatibility of vascular grafts with a  $CF_x$  fluorocarbon coating deposited at the inside wall of the grafts in a proper plasma reactor fed with tetrafluoroethylene ( $C_2F_4$ , TFE) at 0.2 Torr. In the preferred embodiment of the invention no other materials are interposed between the substrate and the coating.

U.S. Pat No 5,328,576 discloses a method for imparting water and oil repellent surface properties to fabrics or paper that includes pretreatment in a low pressure oxygen plasma in the presence of water vapor followed by plasma polymerization of methane in a high frequency glow discharge carried out in the same treatment chamber. This method doesn't deliver durable, permanent coatings with a WCA higher than about 120°.

U.S. Pat. No. 5,262,208 discloses an gas plasma treatment for archival preservation of paper manuscripts by a thin film protective polymer film. The treatment time is ranging from 30-3600 seconds. Other methods have been used to obtain thin coatings on the web materials with short treatment periods. Providing surface treatment is disclosed in US Patent No. 4,842,893 and 4,954,371 which describe a process for high speed coating of substrates with a complete and uniformly adhering layer and using electron beam radiation curing of the vapor deposited monomers for multilayer capacitors. U.S. Pat. No. 4,842,893 discloses high speed coating process including flash vaporization system and electron beam curing. Both of these electron beam disclosures are incorporated herein by reference. Other uses of electron beam coatings in the electronic industry field have been reported by Westinghouse science & technology center USA (Adv. Mat. Newsletter Volume 13, No 9, 1991 page 4).

It has now been found that providing at least part of the surface of textiles with a hydrophobicity at heretoforth unachievable levels can provide a tremendous benefit to the use of such textiles.

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#### Summary of the invention

The present invention relates to textile articles or clothing referred to herein after as textiles, such as outdoor garments, indoor fabrics which are exposed to aqueous liquid such as bed mattresses, carpets, bathroom rugs or the like, swim wear, shoes, leather, hats, textile sun roofs for cars, sun blinds or awnings having at least part of the surface treated to have super hydrophobicity. In particular the present invention relates to textiles which are coated by means of modulated plasma deposition of fluorocarbons.

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Specifically, the present invention, having the features mentioned in the annexed claims, relates to textiles having at least part of their surface coated with a thin, well adherent, nonporous, fluorocarbon coating with super hydrophobic properties, i.e. characterized by static water contact angle (WCA) values, measured on a smooth and plane surface, higher than about 120°, preferably higher than 130°, more preferably higher than 150°. For example, textiles being treated with this method have their hydrophobicity markedly improved. They can for example provide improvements in water repellency, soil/dirt sticking prevention, reduced build-up on surface or not detrimental to water vapour/ air permability.

The present invention deals with textiles having their surface treated i.e. characterized by static water contact angle (WCA) values higher than about 120°, preferably higher than 130°, more preferably higher than 150°.

The textile substrates of interest for the present invention may include a wide range of materials in form of webs, tapes, films, animal skin like leather or fur, woven and non-woven layers; they can be porous or non-porous, rigid or flexible, made of polymers, natural or synthetic fibers, leather, biodegradable materials, or any conventional material used in making textiles or products comprising textiles for outside use.

When organic synthetic resins are chosen, such substrate materials could be fabricated from polyethylene, polyacrylics, polypropylene, polyvinyl chloride, polyamides, polystyrene, polyurethanes, polyfluorocarbons, polyesters, silicone rubber, hydrocarbon rubbers, polycarbonates and other synthetic polymers. A particularly preferred polymeric substrate is polyethylene or polypropylene as used e.g. in the manufacture of non-woven textile substrates.

The textiles are preferably subjected to a modulated glow discharge plasma treatment performed with a fluorocarbon gas or vapor compound fed in a properly configured reactor vessel where the textiles are positioned. The plasma process deposits a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, tightly bound to the surface of the textiles.

Alternatively a more conventional thin film coating process followed by high energy surface curing can be used. This is the method of using a high speed vacuum coating process for producing durable and thin water-repellent coatings on a



textile substrate. It uses e.g. a movable support such as rotating drum in a vacuum chamber. The surface of the support is maintained at a temperature sufficient to permit condensation of a vaporized material deposited in the chamber. The material is a curable monomer with a relatively low molecular weight. The monomer vapor is created using a flash vaporizer. The desired amount of curable monomer is metered to a heated flash vaporizer system where the material is vaporized. It is then transported e.g. by it's inherent pressure, to the textile substrate resting on the rotating drum and condensed on the surface of the textile substrate. According to the method the textile substrate is then transported to a curing means such as an energy source which emits an electron beam, UV-light radiation or exposure to an electro magnetic field. Alternative the curable monomer can also be transferred into radicals by passing through a plasma zone (zone of high voltage discharge). The curing of the monomer by the curing means then provides a coating on the textile substrate surface which has a static water contact angle of more than 120°.

The method for delivering the curable monomer to the textile substrate for minimizing the amount of monomers can use an ultrasonic atomizer producing micro droplets of curable monomer. They are released into a vaporization tube heated by band heaters. The atomized droplets impinge on the inner wall of the vaporization tube and are instantaneously vaporized, i.e., flash vaporized. This reduces the opportunity for polymerization prior to being deposited on the textile substrate.

In one aspect of the present invention, the textile substrate can be one side water-repellent or alternatively be repellent on both sides.

"Plasma," as used herein, is used in the sense of "low-temperature plasma" or "cold plasma" produced by igniting a glow discharge in a low pressure gas through a power supply. Glow discharges contain a variety of species chemically active and energetic enough to cause chemical reactions with surfaces exposed, i.e. covalent bonding to a suitable substrate material. Cold plasmas, or glow discharges, are generally produced with high frequency (from KHz to MHz and GHz) power supply (HF plasmas). Electrons, positive and negative ions, atoms,

excited molecules, free radicals, and photons of various energies are formed in a cold plasma.

5 "Modulated plasma" means a non continuous plasma, HF plasma, i.e. a glow discharge whose driving power is pulsed between a maximum value and zero (ON/OFF pulse) or a fraction of it, at a certain frequency, with a proper pulse generator connected to the main power supply. In the case of ON/OFF pulsed systems, the time ON and time OFF values are among the experimental parameters of the process. Superimposing a triggering ON/OFF pulse to the main  
10 high frequency field which generally drives a glow discharge, alternates short continuous discharges with plasma OFF time intervals where active species still exists in the gas phase, but the effects of ions and electrons are strongly reduced. This alternating exposure to two different processes leads to unique surface modifications of substrates, which can be very different from those of continuous  
15 plasma process, as it will be shown.

"Plasma deposition" or "plasma polymerization" is the plasma process that leads to the formation of thin (0.01 - 2  $\mu\text{m}$ ), partly crosslinked, void-free, continuous coatings well adherent to substrates. The molecules of the gas phase are  
20 fragmented by energetic electrons, which are able to break chemical bonds; this process leads to radicals and other chemical species which are able to deposit at surfaces inside the vacuum chamber and form a thin, uniform film. The action of the plasma may also affect the surface of a polymer substrate in the early deposition time; energetic species may break bonds in the substrate with possible  
25 evolution of gas products, such as hydrogen, and formation of free radical sites which contribute to form covalent bonds between the growing film and the substrate.

It has been found that it is possible to deposit thin fluorocarbon films with super  
30 hydrophobic characteristics, i.e. showing a surprisingly high static water contact angle (WCA) value, even up to about 165°. The present invention thus refers to textiles with fluorocarbon films characterized by a WCA value higher than 120°, preferably higher than 130°, more preferably higher than 150°.

35 In particular fluorocarbon coatings with F/C ratio from about 1.50 to about 2.00 deposited on different substrates and characterized by WCA values higher than about 120°, such as between about 155° and about 165°, find useful application in textiles, especially if the coatings have been deposited at the surface of different

- polymer substrates such as polyethylene (PE), polypropylene (PP) polyethyleneterephthalate (PET), in form of films and/ or nonwovens. It should be noted that the F/C ratio could be theoretically up to 3, if the coating would be formed only by a mono-molecular layer of  $\text{CF}_3$  groups. But the formation of
- 5 intermolecular cross-links and the formation of the claims (containing  $\text{CF}_2$  fragments) which are grafted onto the surface lowers the above theoretical value so that the obtained coatings, notwithstanding the fact that they contain many  $\text{CF}_3$  groups, have a general F/C ratio in the range of about 1.50 to about 2.00.
- 10 The thickness of the coatings depends on the duration of the plasma process at different conditions, and can be kept between 0.01 and 2  $\mu\text{m}$ . It has been found that the nature of the substrate materials does not influence the chemical composition or the thickness of the coatings. Coatings with WCA values up to about  $165^\circ$  (e.g.  $165^\circ \pm 5^\circ$ ) were obtained.
- 15 Textiles to be treated are subjected to modulated plasma gas discharge in the presence of at least one fluorocarbon gas or vapor. Specifically, fluorocarbon gases or vapors such as tetrafluoroethylene ( $\text{TFE}, \text{C}_2\text{F}_4$ ), hexafluoropropene ( $\text{HFP}, \text{C}_3\text{F}_6$ ), perfluoro-(2-trifluoromethyl-)pentene, perfluoro-(2-methylpent-2-ene)
- 20 or its trimer may be used, TFE being the presently preferred choice. The plasma deposition process is preferably performed by positioning the textile in a properly arranged plasma reactor, connecting the reactor to a source of a fluorocarbon gas or vapor, regulating flow and pressure of the gas inside the reactor, and sustaining a glow discharge in the reactor with a high frequency electric field in a pulsed
- 25 (modulated) mode by means of a suitable pulsed power supply. The parameters which define the glow discharge treatment includes the feed gas or vapor, its flow rate, its pressure, the position of the textile inside the reactor, the design of the reactor, the exciting frequency of the power supply, the input power, the time ON and the time OFF of the pulsing system. Textiles may be positioned in the "glow"
- 30 region of the discharge, i.e. directly exposed to the plasma, or in the "afterglow" region, i.e. downstream in respect to the visible glow. The two positions generally result in coatings with different composition and properties; treating the textiles with modulated glow discharge results also in different coatings respect to continuous treatments.

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#### Brief description of the drawings

The invention will now be described, purely by way of example, with reference to

the enclosed figures of drawing, wherein:

- Figure 1 compares a conventional "continuous" RF glow discharge with an ON/OFF "modulated" RF glow discharge;
- Figure 2 portrays a typical scheme of a plasma reactor adapted for use within the context of the invention;
- Figure 3 shows a C1s ESCA signal of an uncoated polyethylene substrate wherein the signal is due only to C-H, C-C bonds of the substrate;
- Figure 4 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, continuous mode), with WCA of  $100 \pm 5^\circ$ ; the signal is composed by components due to CF<sub>3</sub>, CF<sub>2</sub>, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination;
- Figure 5 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (afterglow position, continuous mode), with WCA of  $120 \pm 5^\circ$ ; the signal is composed by components due to CF<sub>3</sub>, CF<sub>2</sub>, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination; and
- Figure 6 shows a C1s ESCA signal of a PE substrate coated with a fluorocarbon coating deposited as described in example 1 (glow position, modulated mode), with WCA of  $165 \pm 5^\circ$ ; the signal is composed by components due to CF<sub>3</sub>, CF<sub>2</sub>, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination.

#### Detailed description of the invention

Figure 1 compares a conventional "continuous" plasma (figure 1a) with the modulated process of the invention, (figure 1b) showing pulsed alternating plasma ON with plasma OFF (i.e. no plasma) times. The two processes are schematized by referring to their driving signals.

The reactor 1 schematically shown in figure 2 was utilized not exclusively for developing the deposition method object of the present invention. The reactor vacuum chamber 1 is made of Pyrex glass, is provided with an external RF powered electrode 2 and an internal grounded electrode 3. The external electrode is connected to a power supply 4 (typically a radiofrequency generator operating at e.g. 13.56 MHz) through a matching network and an ON/OFF pulse generator 5. The textiles can be treated in the "glow" region of the reactor, onto the grounded electrode 3, as well as in its "afterglow" position i.e. at an afterglow

textile holder 6. The gas/vapor is fed through a proper mass flowmeter through a gas/vapor feeding manifold 7, and its pressure, measured at the pump out exit 8 of the reactor, kept at a certain constant value with a manual valve on the vacuum connection between the reactor and its pumping unit. Even though the arrangement shown in the drawing represents a presently preferred choice, those skilled in the art will immediately recognize that pulsed energization of the plasma reactor can be achieved by different means such as direct energization by means of pulsed RF generators commonly used in radar and telecommunication techniques.

10 Preferably, the deposition process is performed with an RF (13.56 MHz) generator. The RF power delivered to the external electrode of the reactor is kept in the 1-500 Watts range for a power density of 0.02-10 Watt/cm<sup>2</sup>. The reactor is fed with a fluorocarbon compound at a 1-100 sccm flow rate and is kept at a constant pressure of 50-1000 mTorr during the process. Preferably, the glow discharges are modulated through the pulse generator, preferably at 1-500 ms time ON and 1-1000 ms time OFF values, with respective values of about 10 ms and about 190 ms being the most preferred choice at present. The deposition process may range from a few seconds to many hours; during this time a uniform fluorocarbon coating is deposited on the textiles positioned in the glow as well as on those in the afterglow region. The deposition rate, a typical one being in the 20 - 400 Å/min range, was measured by weighing (weight/time) the textiles before and after the discharge, or by measuring the thickness of the coatings (thickness/time) with an Alpha Step profilometer. The deposition rate and the chemical composition of the coating depend on the experimental conditions (pressure, power, textile position, time ON, time OFF, gas feed and flow rate) of the discharge.

The coatings obtained are uniform over the entire surface of the textile; when deposited on flat (i.e. plane), smooth substrates, their hydrophobic character has been estimated through their static WCA value, as measured with a WCA goniometer. The measurement is done on a flat, i.e. plane, and smooth surface of a substrate after coating. The term smooth as used herein for water contact angle measurements refers to a roughness of no more than 5 microns in accordance with standard roughness measurements on continuous surfaces. WCA values in the range about 120° to about 165°, corresponding to a critical surface tension lower than that of PTFE (18 dynes/cm) have been measured for fluorocarbon CFx

coatings, when  $x$  ranges between about 1.50 and about 2.00. The chemical composition of coatings is preferably determined by Electron Spectroscopy for Chemical Analysis (ESCA) within the sampling depth of the technique (about 100 Å). The adherence of the coating to the textile is very good.

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The following examples are given for the purpose of still better illustrating the inventive concept of the present invention, and for highlighting the advantages of using modulated over continuous treatments.

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#### EXAMPLE 1

Three sets of plane and smooth substrates of silicon, PE and PP, of areas in the range of 2-10 cm<sup>2</sup> per material, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of substrates was positioned in the afterglow position at 6. C<sub>2</sub>F<sub>4</sub> was set to feed continuously the reactor at 6 sccm, and the pressure set at 300 mTorr. The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 90 min, then switched off.

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Another glow discharge was subsequently run with a similar set of substrates positioned in the glow position and no substrates in the afterglow position, under the same conditions described above except for the fact that modulation was effected at 10 ms time ON and 190 ms time OFF through the pulse generator.

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At the end of the two discharges the substrates were extracted from the reactor and their WCA measured. The WCA values shown in Table 1 were found, which are compared to the WCA values of the unprocessed substrates. A deposition rate of  $30 \pm 5$  Å/min was measured for the coatings deposited in the modulated mode.

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Other substrates, treated in the two modes, were analyzed with the ESCA technique. Their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 2a-c. No other elements were detected (e.g. Si for silicon substrates), which means that the coatings are continuous. The C1s spectrum of the uncoated PE substrate is shown in Figure 3, while the C1s spectra of PE samples coated as described above are shown in Figures 4, 5 and 6, respectively.

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Table 1

SUBSTRATE	Si	PE	PP
WCA unprocessed	$15^{\circ} \pm 3^{\circ}$	$95^{\circ} \pm 3^{\circ}$	$85^{\circ} \pm 3^{\circ}$
WCA continuous discharge (glow position)	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$
WCA continuous discharge (afterglow position)	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$
WCA modulated discharge (glow position)	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$

5 Table 2a

ESCA results for the continuous discharge (glow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	43.3	42.4	42.9
fluorine atomic %	56.7	57.6	57.1
F/C ratio	1.31	1.36	1.33

Table 2b

10 ESCA results for the continuous discharge (afterglow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	34.4	33.8	34.1
fluorine atomic %	65.6	66.2	65.9
F/C ratio	1.91	1.96	1.93

Table 2c

ESCA results for the modulated discharge (glow position) of Example 1

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COATED SUBSTRATE	Si	PE	PP
carbon atomic %	36.4	36.2	36.7
fluorine atomic %	63.6	63.8	63.3
F/C ratio	1.75	1.76	1.72

These examples were made on smooth and plane surfaces for Laboratory convenience and measurement of the WCAs. The respective textile surface e.g. if fibrous may have an apparent WCA which differs from the plane and smooth surface WCA due to the surface texture. However the microscopic surface behavior due to the coating is not different from fibers to plane, smooth surfaces.

As an alternative to provide the textile substrates of the present invention the method of thin film coating with a monomer followed by surface curing can be used.

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The coating formed by the method of the present invention has a thickness of less than 5 microns, and preferably less than 2 microns and most preferably in the range of 0.001 to 1 microns. The coatings are formed by depositing a vapor of curable monomer, under vacuum, on a movable textile substrate which is mounted in thermal contact with a support, for continuous processing preferably a rotating drum, which is maintained at a temperature below the boiling point of the vaporized monomer under the environmental conditions in vacuum chamber. As a result of this temperature differential, the monomer vapor condenses on the surface of the textile substrate. The monomer materials utilized in the present invention are relatively low in molecular weight, between 150 and 1000 Atomic Mass Units (AMU), and preferably in the range 200 to 300 AMU. Polyfunctional fluoroocarbons and especially fluoroacrylates or mixtures of monofunctional fluoroacrylates and polyfunctional fluoroacrylates are preferred. The monomers or monomer mixtures employed have an average of about two or more double bonds (i.e., a plurality of olefinic groups) and have a vapor pressure such that they condense on the textile substrate surface. Such vapor pressures are for example pressure between about  $1.33 \cdot 10^{-6}$  mbar and  $1.33 \cdot 10^{-1}$  mbar, most preferably a vapor pressure of approximately  $1.33 \cdot 10^{-2}$  mbar at standard temperature and pressure, (i.e., relatively low boiling materials) are selected.

30

These high-vapor-pressure monomers can be flash vaporized already at low temperatures and thus are not degraded (cracked) by the heating process. The absence or low amount of unreactive degradation products results in coatings with a reduced levels of volatile components in which substantially all of the deposited



monomer is reactive and will cure to form an integral film when exposed to a source of radiation. These properties make it possible to provide a substantially continuous coating despite the fact that the deposited film is very thin. The cured films exhibit excellent adhesion and are resistant to chemical attack by organic solvents and inorganic salts.

The high speed vacuum coating process for producing water vapour permeable textile substrates with exceptional water repellent properties require a curable monomer component. Desirably, the curable monomer for obtaining water-repellent coatings comprises fluoro-containing group.

In one embodiment, any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoro olefin monomers, fluorostyrene monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

In one embodiment, fluorostyrenes and fluorinated vinyl alkyl ether monomers which may be used in the method of the present invention include, but are not limited to,  $\alpha$  -fluorostyrene;  $\beta$  -fluorostyrene;  $\alpha$ ,  $\beta$  -difluorostyrene;  $\beta$ ,  $\beta$  -difluorostyrene;  $\alpha$ ,  $\beta$ ,  $\beta$  -trifluorostyrene;  $\alpha$  -trifluoromethylstyrene; 2,4,6-Tris (trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro-  $\alpha$  -methylstyrene; and 2,3,4,5,6-pentafluoro-  $\beta$  -methylstyrene.

In yet another embodiment, tetrafluoroethylene can also be used in the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-perfluorovinyl ether copolymers (e.g., copolymers of tetrafluoroethylene with perfluoropropyl vinyl ether), tetrafluoroethylene-ethylene copolymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

In still another embodiment, fluorocarbon elastomers (see, e.g., 7 Encyclopedia of Polymer Science & Engineering 257) are a group of fluoro olefin polymers which can also be used in the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-co-hexafluoropropylene); poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene); poly[vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-co-propylene); and poly(vinylidene fluoride-co-chlorotrifluoroethylene).

10

In the preferred embodiment, because of their reactivity, physical properties, and the properties of cured films formed from such components, fluoroacrylates are particularly useful monomeric materials. The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ( $H_2C = CHCOOH$ ) or methacrylic acid ( $H_2C = CCH_3 - COOH$ ), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I):  $H_2C = CR_1 - COO (CH_2)_n R_2$  (I) wherein: n is 1 or 2;

15

$R_1$  is hydrogen or methyl; and  $R_2$  is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated  $C_1$  to  $C_{10}$  alkyl, phenyl, or naphthyl.

20

In a particular embodiment of the invention,  $R_2$  is a  $C_1$  to  $C_8$  perfluoroalkyl or  $-CH_2 - NR_3 - SO_2 - R_4$ , wherein  $R_3$  is  $C_1$ - $C_2$  alkyl and  $R_4$  is  $C_1$  to  $C_8$  perfluoroalkyl. The term "perfluorinated," as used herein, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine. Monomers illustrative of Formula (I) above, and their abbreviations, include the following:

25

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");

2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");  
2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");  
1,1-Dihydroperfluorooctyl acrylate ("FOA"); and  
1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

5

Alternatively, the curable monomer component can also include polyfunctional acrylates, which are set forth in U.S. Patent 4,842,893.

#### Benefits of the present invention

10

Without wishing to be bound by theory it is believed that the benefits of the present invention are obtainable by the mechanism indicated below. Textiles according to the present invention are providing usually several functions. For one they are protective to the respective wearer. In addition they need to provide  
15 comfort and preferably should be such that they do not require special efforts for cleaning and maintenance.

These functions can be drastically improved when considering the superhydrophobic coating on such textiles. For example when providing the  
20 outside of an outdoor garment with such superhydrophobic coating its breathability is not diminished while the probability of rain water entering the garment is drastically improved. This benefit is not only used on garments but of course also on other apparel such as swim wear, shoes and hats as well as various materials such as fabrics or leather or synthetic materials. In addition it can be used for  
25 items which are intended to provide water repellency or impermeability particularly against rain water. Such textiles would be used for umbrellas, tents, marquees, protective canvas coverings, sunroofs in cars or awnings. The coating according to the present invention does not alter the water vapour and (if present), airpermeability of the textiles but reduces or even eliminates the possibility of  
30 liquid water to pass through. This is achieved by several means. First of all the hydrophobic coating as such reduces the contact surface between a drop of water and the textile due to the surface tension of the liquid. In addition however typically such textiles have no absolute horizontal surfaces and use gravitational force to allow liquid to run off. With the superhydrophobic coating according to the present  
35 invention this run off is drastically accelerated such that time during which an amount of liquid could penetrate into the textile is reduced. At the same time such textiles will also dry much faster. Especially when accepting that they become wet,

as e.g. in swim wear, the superhydrophobic coating will cause a substantially faster drying and even render changing of the wet clothes superfluous. E.g. children's swim suits should usually be removed in order to prevent longer term kidney or urinary problems or sand/soil clinging to wet parts of the suit. In contrast  
5 swim suits using superhydrophobic coating do not require this any longer.

In addition to the above benefits it is also note worthy to mention that textiles permanently used outside with superhydrophobic coating have a reduced tendency of being soiled. When considering how soils and dirt are transported  
10 onto textiles surfaces it is clear that a reduction in the attraction between the dirt and the surface alone can provide a benefit but in addition the accelerated run off will also have a higher probability of transporting already deposited dirt away.

Finally liquid which remains on the surface contains usually a certain amount of  
15 solid material which after evaporation of the water remains on the textile surface. With an increase probability of run off of such liquids the amount of deposited residue on the textiles surface is also reduced to the superhydrophobic coating.

Claims

1. A textile article is characterized in that at least part of the surface of said  
5 article is surface treated with a coating and said coating renders a plane and  
smooth treated surface to have a static water contact angle (WCA) higher than  
about 120°, preferably higher than about 130°, most preferably between about  
150° and about 165°.
- 10 2. A textile article according to claim 1 characterized in that said coating is a  
fluorocarbon coating.
3. A textile article according to claim 2 characterized in that said coating  
exhibits a fluorine/carbon ratio (F/C) of between about 1.50 and about 2.00,  
15 preferably between about 1.60 and about 1.95.
4. A textile article according to any of the preceding claims which article is  
water vapour permeable.
- 20 5. A textile article according to claim 4 characterized in that said article is an  
outdoor garment.
6. A textile article according to claims 1 to 3 wherein said article is a sun roof  
for a car or a sun blind or awning.
- 25 7. A textile article according to claims 1 to 3 wherein said article is a swim  
wear article.

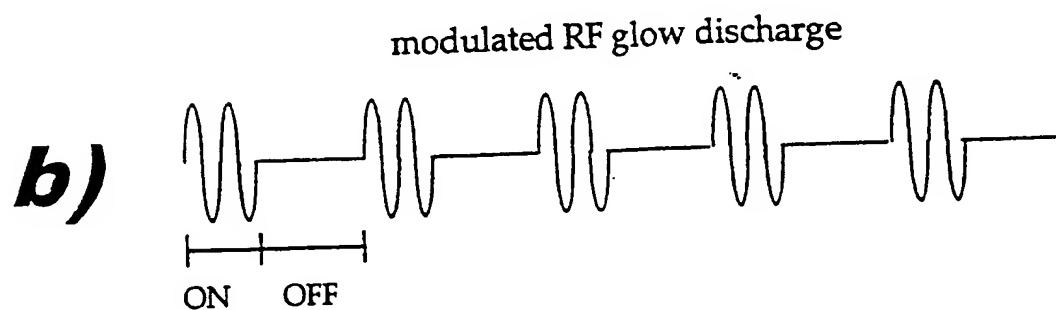
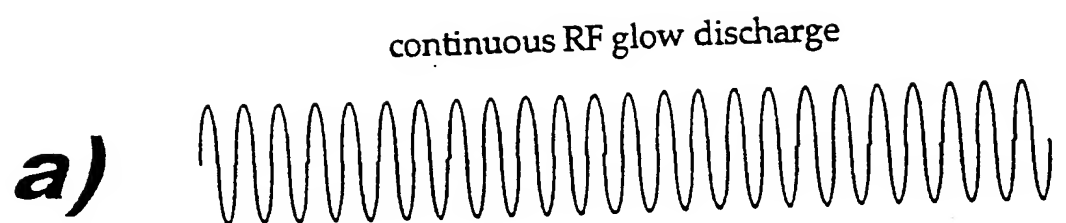


Figure 1

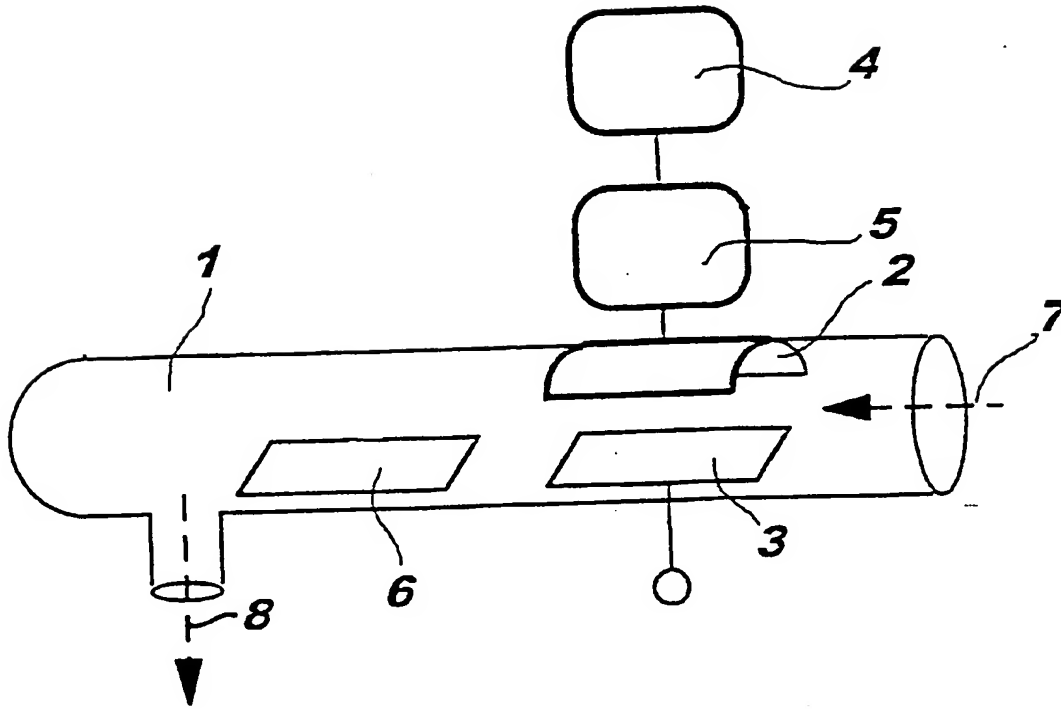
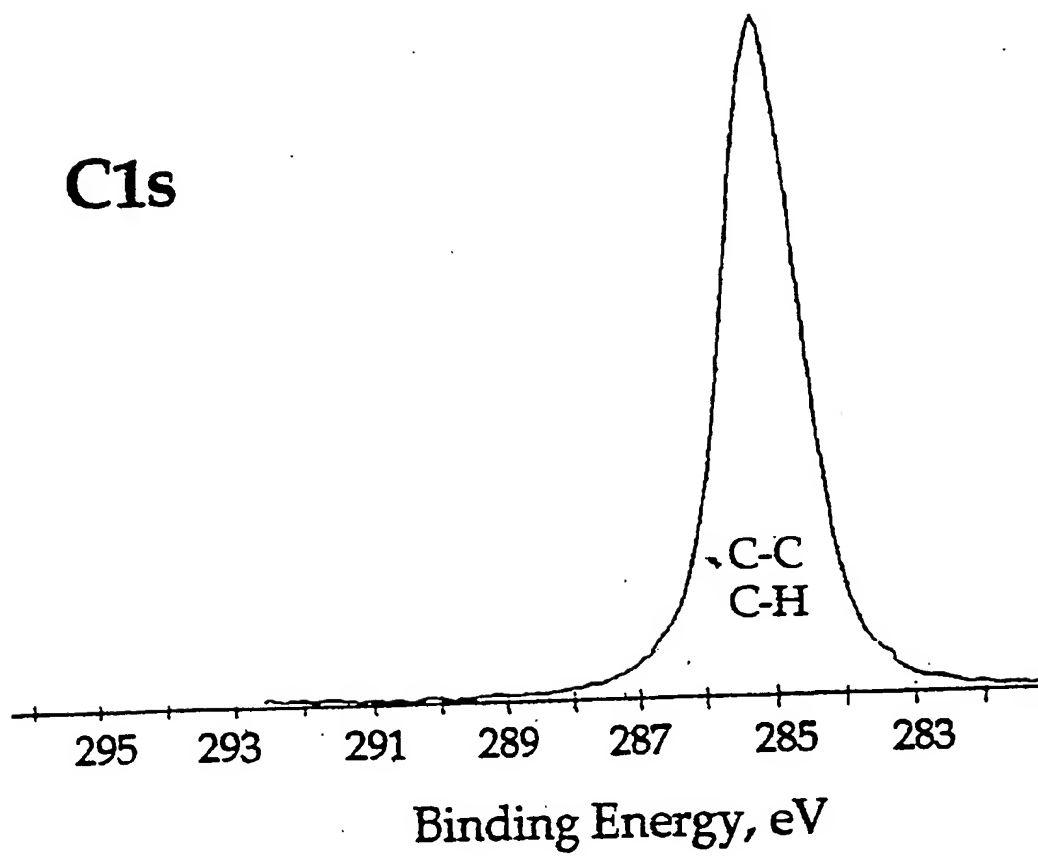


Figure 2



**Figure 3**



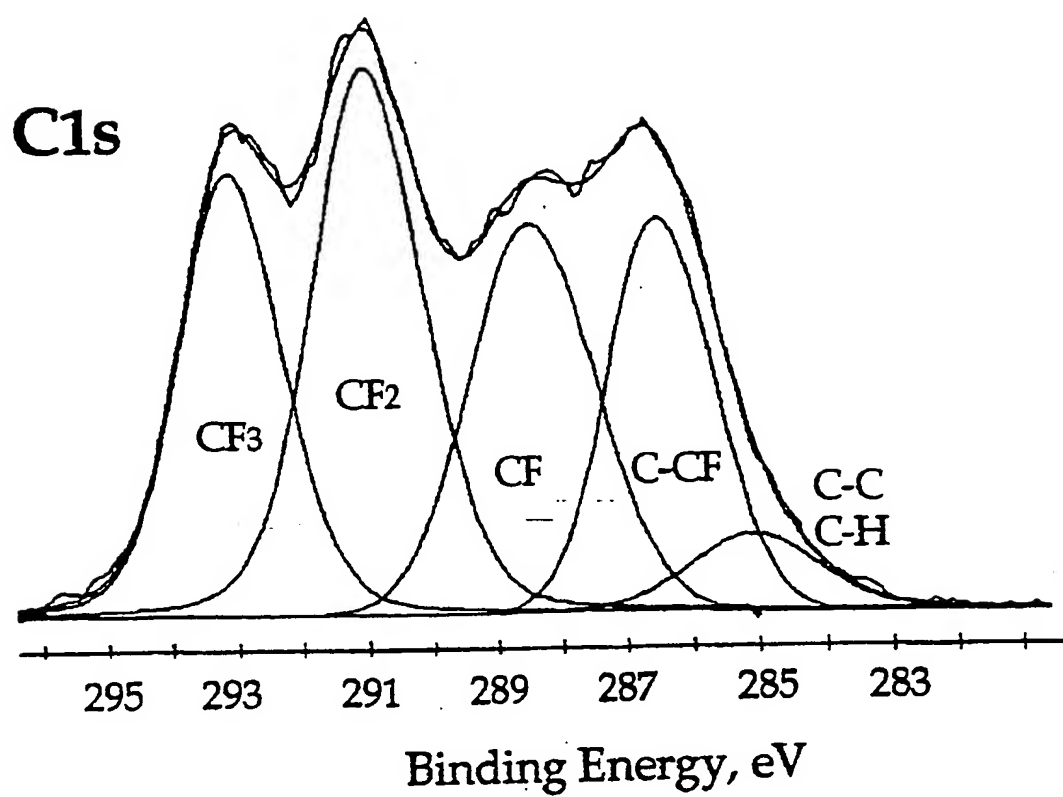


Figure 4

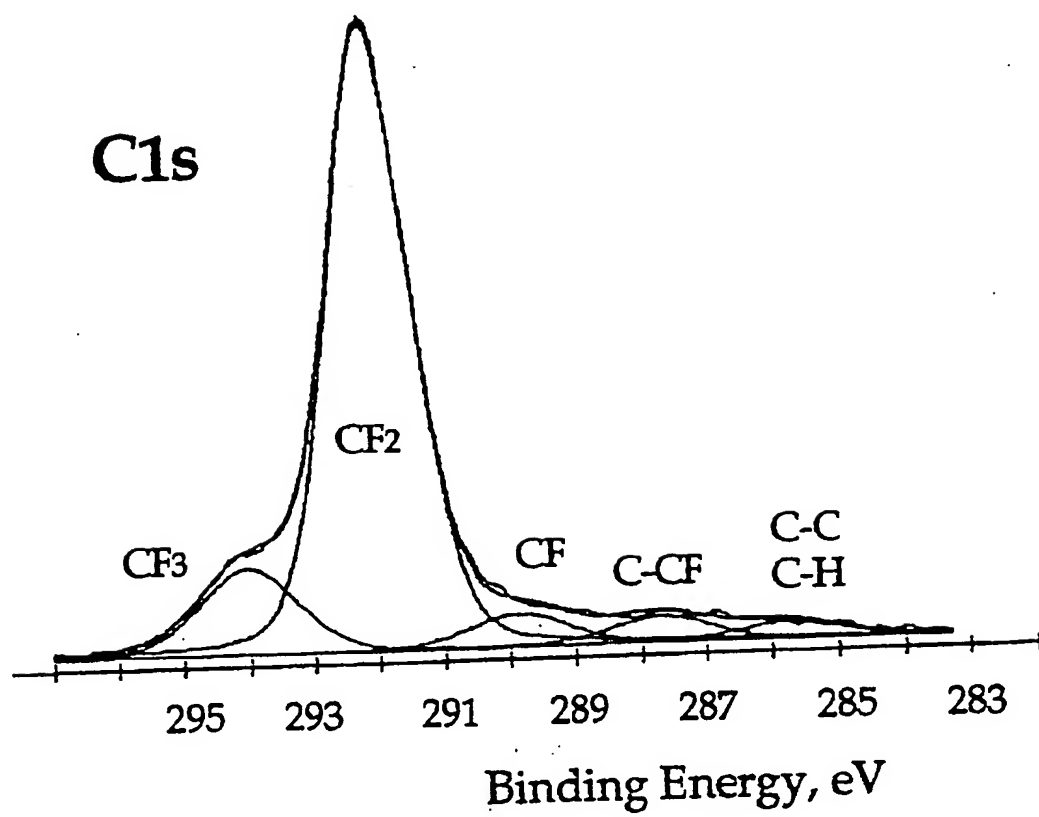


Figure 5

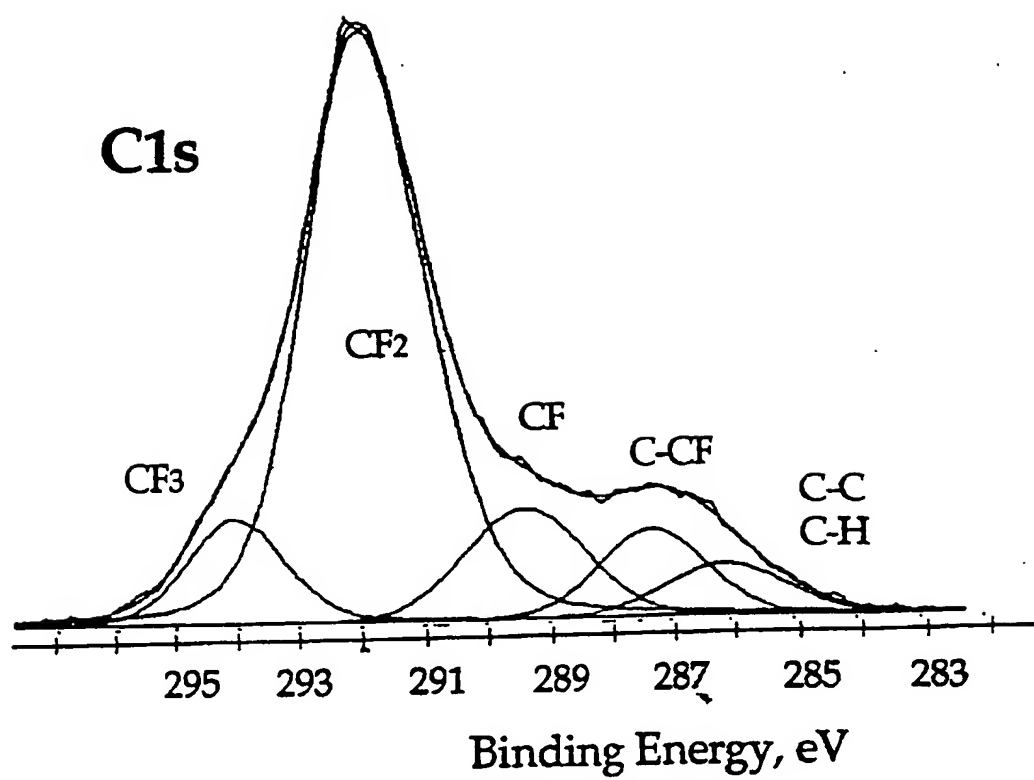


Figure 6

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 99/20926

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D06M10/02 C23C16/30

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 D06M C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 632 842 A (KARWOSKI THEODORE ET AL) 30 December 1986 (1986-12-30) column 3, line 3 - line 18; examples 1,2 column 12, line 1 - line 24 ---	1-4
X	EP 0 508 136 A (MATSUSHITA ELECTRIC IND CO LTD) 14 October 1992 (1992-10-14) examples 1,3,4 ---	1,4,6,7
A	US 5 164 252 A (MECKEL WALTER ET AL) 17 November 1992 (1992-11-17) column 4, line 3 - line 9 -----	1,6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search

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information on patent family members

Int: onal Application No

PCT/US 99/20926

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